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Synthetic Fuels and Biofuels: Questionable Replacements for Petroleum

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SYNTHETIC FUELS AND BIOFUELS: QUESTIONABLE REPLACEMENTS FOR PETROLEUM

1.0 STATEMENT OF THE PROBLEM

Petroleum-derived fuels meet the stringent military requirements that other alternative energy sources cannot [1]. Thus the DOD has a vested interest in maintaining this supply by developing synthetic hydrocarbon fuel from the vast natural resources of the United States such as coal, shale, biomass, gas hydrates, and CO₂ [2].

Any hydrocarbon fuels derived by commercial processes, such as Fischer-Tropsch (FT), and biodiesel fuel will likely be first introduced into the Navy through blends with petroleum fuels [3]. Extensive data exists on the composition of a wide range of petroleum fuels, commercial FT derived fuels, and biofuels [3-7]. However, the blend data of FT with petroleum and biodiesel that does exist is intended to meet commercial requirements and not Navy marine specifications. For example, lubricity issues that may be addressed to the satisfaction of commercial use may not meet the water separation demands of Navy use. Similar issues arise with fuel stability. The satisfactory production of stable fuels for most commercial applications will almost certainly not meet stringent Navy storage requirements [8,9]. In order to guarantee ample fuel reserves necessary for combat operations, the U.S. Navy maintains facilities for storage of mobility fuels for extended periods of time (1-3 years), in regions that differ vastly in climate and storage conditions [10,11]. The storage stability specification for ship propulsion fuel (MIL-PRF-16884L) is just one measure to ensure the combat readiness of the fuel [8].

With the anticipation of synthetic fuel and biodiesel entering the fuel supply, there is concern about the relative stability of FT fuel, biofuel, and their blends with petroleum [12]. Specifically storage stability, hydroperoxide generation, gum formation, and bio fouling (instability, solubility, and emulsification) reactions. This report summarizes the storage stability results found for a stable petroleum fuel and its blends with biodiesel and FT diesel.

2.0 BACKGROUND

The world market supply of oil along with growing environmental concerns has led to an increase demand in production of biodiesel products for blends with petroleum. Recently, the American Society of Testing and Materials (ASTM) approved specifications to include up to 5% biodiesel (B5) in the conventional petroleum diesel specification (ASTM D975). Thus petroleum fuel containing up to 5% biodiesel will enter into the U.S. commercial market without it having to be disclosed upon purchase [12].

Naval distillate fuel (F-76) is procured in accordance with MIL-PRF-16884L, which differs from the ASTM D975-06 specification for diesel fuel oils as shown in Table 1 [8,9], in addition to key property requirements that are specific to the Navy [8]. One such property unique to the Navy is storage stability. Due to the Navy's large strategic petroleum reserve, a fuel could be

stored for 1 to 3 years. With the anticipation of B5 entering the fuel supply, concerns have been raised about the relative stability of the blended diesel fuel for Navy Marine Corps use [12].

Table 1. General Properties Required by Specifications for Commercial Diesel, Military Diesel, and Alternative Diesel.

| Property | Military MIL-PRF-16884K | ASTM (D975) Grade Low Sulfur no. 1-D | ASTM (D975) Grade Low Sulfur no. 2-D | Soy-Biodiesel | FT-Diesel |
|--|-------------------------|--------------------------------------|--------------------------------------|---------------|-----------|
| Viscosity at 40 °C, mm ² /s | 1.7 - 4.3 | 1.3 - 2.4 | 1.9 - 4.1 | | |
| Sulfur content, wt. % (max) | 0.5 | 0.05 | 0.05 | 0 | 0.04 |
| Flash point, °C (min) | 60 | 38 | 52 | 218 | 63 |
| Cloud point, °C (max) | -1 | | | | |
| Pour point, °C (max) | -6 | | | | -12 |
| Hydrogen content, wt. % (min) | 12.5 | | | 12.3 | |
| Cetane number, (min) | 42 | 40 | 40 | 45 | 76 |
| Carbon residue, 10% bottoms, wt. % (max) | 0.20 | 0.15 | 0.35 | | |
| Storage Stability, total insolubles, mg/100 mL (max), ASTM D5304 | 3.0 | | | | |
| Trace Metals, ppm (max) Calcium, Lead, Sodium + Potassium, Vanadium | 1.0, 0.5, 1.0, 0.5 | | | | |

In this context, fuel stability refers to the resistance of a fuel to undergo deleterious chemical changes during storage or use. These chemical changes can have an impact on both the physical and chemical properties of the fuel. These chemical processes can lead to changes in color; the development of insoluble reaction products, including soluble and adherent gums, sediments, and other thermal deposits; changes in combustion, and changes in compatibility with other fuels [13]. This can lead to engine system fouling, clogged filters and, fuel lines, and an overall loss in engine performance [13,14].

In addition to biodiesel entering the U.S. commercial supply, significant work is being conducted on the certification of Fischer-Tropsch (FT) fuel and FT fuel blends for use in military applications. Results have indicated that FT-fuels produce very high levels of hydroperoxides and gum during long-term storage stability testing [4]. An approved antioxidant, 2,6-di-tert-butylphenol, was found to be very effective in increasing the long term storage stability of the fuels. When the FT fuels were blended with a stable petroleum jet fuel containing an antioxidant, the overall long term storage stability of the FT fuels was improved [4]. The studies served to demonstrate the potential stability issues that may arise for the Navy and the potential of currently used antioxidants to mitigate the problem [3].

Though antioxidants have proven effective in reducing hydroperoxide and gum formation in FT fuel and their blends, other issues may arise concerning bio fouling reactions when FT fuels are combined with petroleum fuels containing any fraction of biodiesel. For example studies have shown that biodiesel blends with petroleum cannot be used in marine environments where seawater compensating fuel tanks are involved, because at the oil water interface a heavy soapy emulsion forms [6,7]. This layer would plug nozzles, filters, and damage engine parts with the ingestion of the seawater in the heavy emulsion layer. In addition recycled biodiesel blended with stable petroleum fuel can induce instability in the fuel [7]. These fuels were found to have acidic components remaining that were not methylated during the remanufacturing process. Previous studies have shown that a few ppm of carboxylic acids can induce instability reactions in stable diesel fuel [15,16]. **Thus, from a Navy perspective the degree of problems that could arise with the introduction of alternative fuel with petroleum as blends is not yet known with any certainty.**

3.0 EXPERIMENTAL

General Methods. Unless otherwise stated, chemicals were reagent grade and were obtained from commercial sources and used without additional purification.

Storage Stability Tests. The biodiesel-petroleum fuel blends were tested for storage stability and chemical instability reactions. They were tested by a gravimetric technique described in ASTM D5304-99 [17]. A brief description of this method is: 100 mL sample of the blends in 125 mL borosilicate brown glass bottles were subjected to a 16 hour, 90°C time-temperature regimen at 100 psig over pressure of pure oxygen. After the reaction period, the samples were cooled to room temperature. The samples were filtered and the sediment determined by a gravimetric method.

Fischer-Tropsch Diesel Fuel. A large South African Company supplied the FT middle distillate fuel used in this study. This fuel was from coal and distilled to meet the petroleum middle distillate boiling range as shown in Table 1 [9]. A gas chromatography/mass spectrometry (gc/ms) analysis of the particular fuel revealed that it consisted of C₁₁ to C₂₀ alkanes with no aromatic compounds detected. This fuel sample met the MIL Spec. requirements as depicted in Table 1 [8].

Soy Derived Biodiesel Fuel. Ag Environmental Products, 9804 Pflumm Road, Lenexa, KS 66215, supplied soy-derived biodiesel. This material was light yellow in color, had a boiling point greater than 400°F, negligible water solubility, a specific gravity of 0.88, a flashpoint of 425°F and a cetane number > 40. The specific methyl ester concentration in the fuel was determined by gc/ms and illustrated in Table 2.

Mass Spectrometry. The soy fuel and FT fuel were both analyzed by combined capillary column gas chromatography/mass spectrometry, gc/ms. The gc/ms system consisted of a Hewlett-Packard 5890 Series II gas chromatograph configured for split flow injection (3:1), and a Hewlett-Packard 5971 Series Mass selective detector. The gc was equipped with an all glass

inlet system in conjunction with a 0.20 mm x 50 m polydimethylsiloxane capillary column (HP-1, 19091Z-105) made by Agilent Technologies. The injector temperature was 250°C and the detector temperature was 280°C. The column flow was 1 mL/min. The temperature program started with an initial temperature of 60°C for 3 min, a ramp of 3°C/min, to a final temperature of 290°C that was held for 2 min. A solvent delay of 5 min was also incorporated into the temperature program. The mass spectrometer was operated in the electron impact ionization mode (70 eV) with continuous scan acquisition from 35 to 550 amu at a cycling rate of approximately 150 scans/sec. The parameters were set up with the electron multiplier at 1212 V. These gc/ms parameters provided excellent separation of the compounds in the soy-derived fuel. The HP, MS Chem Station Hardware 61701BA version B.01.00 was used to process mass spectral information.

Table 2. Methyl Esters Concentration in Soy-Derived Biodiesel

| Methyl Ester | Carbon Number | Concentration ^a (wt%) |
|-------------------|-----------------|----------------------------------|
| methyl linoleate | C ₁₈ | 53 |
| methyl oleate | C ₁₈ | 24 |
| methyl stearate | C ₁₈ | 10 |
| methyl palmitate | C ₁₆ | 10 |
| methyl linolenate | C ₁₈ | 3 |

^aTraces of other unidentified methyl esters.

4.0 RESULTS

Soy biodiesel was blended with both petroleum and a FT diesel fuel and examined for fuel instability reactions. Military fuel unlike fuel in the civilian sector is stored for 1 to 3 years all over the world [10,11]. Under these conditions, the fuel can react with oxygen, other molecules (in the fuel) and water from the air [16,18]. Fuel instability is defined as the formation of insoluble sediments and expressed as mg/100 mL fuel [17]. Sediments once formed can plug fuel filters, nozzles, injectors and cause severe mechanical damage. NRL developed an ASTM test method (ASTM D5304) for the gravimetric determination of these insolubles [17], and the method gives results measured in milligrams of solids/100 mL of fuel. By this procedure, 2.0 mg of sediment/100 mL fuel or less is indicative of a fuel that will be stable in bulk tank storage for at least two years. The results in Table 3 show that soy biodiesel can be safely blended with petroleum diesel in an amount up to four times (20%) currently approved (5% blend) in the conventional petroleum diesel specification.

Table 3. Storage Stability of Petroleum and Fischer-Tropsch Derived Fuels and Soy-Biofuel Blends.

| Fuel | Gravimetric Solids in mg/100 mL fuel |
|---|--------------------------------------|
| 100 mL Petroleum Diesel | 0.1 |
| 100 mL (FT) Diesel | 0.4 |
| 50 mL Petroleum + 50 mL FT | 1.7 |
| Soy Fuel Blends | |
| 10 mL Soy in 90 mL Petroleum Diesel | 0.3 |
| 20 mL Soy in 80 mL Petroleum Diesel | 0.2 |
| 5 mL Soy in 47.5 mL Petroleum Diesel + 47.5 mL FT | 79.8 |
| 5 mL Soy + 95 mL FT | 735.0 |

Similarly the results for FT and FT blends with petroleum diesel show FT fuel can be blended with petroleum up to 50% by volume. **While the FT fuel and FT fuel blends with petroleum pass the ASTM stability test, the results in Table 3 show that FT blends with biofuel fail the stability test.** A 5% biofuel 95% FT blend (v/v) produced large amounts of sediments, 735 mg of solids. Figures 1 and 2 are pictures of the filter media after the FT and FT blend with biodiesel are aged and passed through the material. The FT fuel alone only produced 0.4 mg of sediment/100 mL of fuel and the filtering material is relatively clear as shown in Figure 1. When combined with any fraction of biodiesel up to 5 mL, the sediment formation is very evident on the filtering media as shown in Figure 2.



Figure 1. Filtering material after contact with stressed FT fuel.

Once these studies were completed, it was noted that when the biofuel was added originally to the FT fuel, the soy biofuel settled to the bottom of the reaction flask. Even at temperatures and pressures of the ASTM method, the biofuel appears to be insoluble in the FT fuel. Further analysis of the FT fuel by gc/ms explains the insolubility of the biofuel. The FT fuel is non-polar and consists of 100% alkanes (straight and branched). The composition of this fuel is

significantly different than that of a typical petroleum derived middle distillate fuel, which contains 60% or more aromatic compounds.

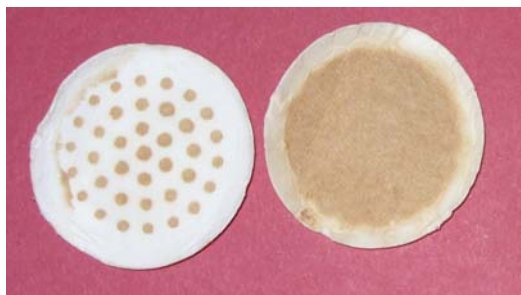


Figure 2. Filtering material after contact with stressed 47.5% FT blend with 47.5% petroleum and 5% biodiesel.

The results found for FT fuel and petroleum middle distillate fuel that contained 5% soy-biofuel as shown in Table 3, indicate that the stability of the blend is better than that observed in the FT fuel alone, by a factor of about 10, but still a significant failure at 80.0 mg/100 mL fuel. It is clear from the results that the aromatic content of the blend with petroleum increased the solubility of the biofuel by 90%, however it was not enough to render the fuel blend stable.

5.0 CONCLUSIONS

The blending of various fuels must be done with great caution. The results from this study showed that this particular FT fuel was not compatible with soy-derived biofuels. Even at low concentrations, 5%, and elevated temperatures and pressures, the biodiesel appeared insoluble when blended with FT and an FT petroleum middle distillate blend. This insolubility produced a large yield of sediments in the ASTM storage stability test. This insolubility means that all of the FT blends with biofuel could potentially lead to mechanical issues with a ships' propulsion system and most certainly could not be stored and be used as diesel fuels for combat operations. **This has significant relevance to the Navy as 5% biodiesel is entering the commercial market, and the certification of FT fuels and FT fuel blends with petroleum middle distillate fuel for military applications is underway.**

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